A composition for surface treatment of aluminium, aluminium alloy, magnesium or magnesium alloy and the treating solutions being diluted to the desired concentration are defined. A said composition containing (1) compound A containing at least one metal element from the group consisting of Hf(IV), Ti(IV) and Zr(IV), (2) fluorine containing compound of sufficient amount to make fluorine existed in the composition at least 5 times of molarity to the total molarity of metal contained in above mentioned compound A, (3) at least one metal ion B selected from the group of alkaline earth metals, (4) at least one metal ion C selected from the group consisting of Al, Zn, Mg, Mn and Cu, and (5) nitric ion and the mol concentration of compound A is 0.1-50 mmol/L as metal element of Hf(IV), Ti(IV) and Zr(IV).

The metal treated with the treating method applying the present invention solution has excellent resistance to various corrosive environments.
TREATING LIQUID FOR SURFACE TREATMENT OF ALUMINUM OR MAGNESIUM BASED METAL AND METHOD OF SURFACE TREATMENT

FIELD OF THE INVENTION

[0001] The present invention relates to a composition for surface treatment used for the purpose to deposit a surface treated film giving good resistance against the corrosion environment to metals such as aluminum or aluminum alloy, magnesium or magnesium alloy in which these metals are used without coating or better resistance to corrosion environment not discharging waste e.g. hexavalent chrome, a treating solution for surface treatment and a method for surface treatment. The present invention further relates to a treated metal material which has excellent corrosion resistance to various environment.

DESCRIPTION OF THE PRIOR ART

[0002] Aluminum and aluminum alloy are applied increasingly in the field of car parts industry to lighten a car. For example, for cylinder head cover, cylinder head, crank case and timing gear case, which are the parts connecting with engine, aluminum alloy die cast e.g. ADC10 or ADC12 are used and 5000 alloy or 6000 alloy are used. Currently the magnesium and magnesium alloy are also used from the same viewpoint.

[0003] Furthermore, aluminum, aluminum alloy, magnesium and magnesium alloy are applied in other fields than car body. And the conditions of use for these metals and metal alloys are variable, namely, sometimes used with coating after molded and sometimes used without coating. Therefore, the functions necessary for surface treatment are variable, and the functions which meet to the exposing atmosphere, for example, adhesion or corrosion resistance of uncoated metal and corrosion resistance after coated are required.

[0004] As the surface treatment to be performed on aluminum, aluminum alloy, magnesium and magnesium alloy, a chromate treatment using hexavalent chrome is popular. The chromate treatments can be classified to two types, one contains hexavalent chrome in film and the other one does not contain hexavalent chrome in film, however both treatment contain hexavalent chrome in the waste solution. Therefore, this chromate method is not so desired from the view point of environmental regulation.

[0005] As the surface treating method not using hexavalent chrome is, a zinc phosphate treatment. For the purpose to deposit a zinc phosphate film on the surface of aluminum, aluminum alloy, magnesium and magnesium alloy, various inventions were proposed. For example, in JP6-99815 publication, the method to deposit zinc phosphate film, which has excellent corrosion resistance, especially scab corrosion resistance after cathodic electrodeposition coating is proposed. This method is characterized by regulating the concentration of fluorine in zinc phosphate film treating solution, further by regulating molar ratio of complex fluoride to fluorine and the concentration of activated fluorine measured by a silicon electrode meter into a specific limitation.

[0006] Further, in JP3-240972A Laid Open Publication, the method to form a zinc phosphate film, which is excelling in the corrosion resistance and especially in scabbing resistance after cathodic electrodeposition coating is proposed. This method is characterized by regulating the concentration of fluorine, keeping lower limit of molar ratio of complex fluoride to fluorine and using zinc phosphate treating solution in which activated fluorine concentration measured by a silicon electrode meter is kept into a specific limitation. Adding to this operation, aluminum ion is precipitated from said zinc phosphate treating solution by adding fluorine after said zinc phosphate treating solution is introduces in the outside of a zinc phosphate treating bath.

[0007] These methods are aiming to improve the zinc phosphate treatment ability to aluminum alloy by increasing the fluorine ion concentration in zinc phosphate treating solution. However, it is difficult to obtain good corrosion resistance of uncoated metal by zinc phosphate film, further, since aluminum ion solved out at the zinc phosphate treatment causes the increase of the waste product by forming sludge.

[0008] In JP6-330341A Laid Open publication, discloses the zinc phosphate treating method for magnesium alloy. Said method is characterizing by containing specific concentration of zinc ion, manganese ion, phosphate ion, fluoride and an accelerator for film depositing and by keeping upper limits of concentration of nickel ion, cobalt ion and copper ion. Further, in JP8-134662A Laid Open publication, the method to remove the settle out magnesium ion by adding fluorine to the zinc phosphate treating solution for magnesium.

[0009] Above mentioned methods are both aiming the substrate treatment for coating, therefore it is difficult to obtain sufficient corrosion resistance of uncoated metals by a zinc phosphate film. Furthermore, as shown in JP8-134662A Laid Open publication, the generation of sludge, can not be avoided as long as a zinc phosphate treatment is used. The method to form a surface treated film having good adhesion and the corrosion resistance after coating without containing hexavalent chrome in the treating solution except the zinc phosphate treatment, the surface treating solution for aluminum or aluminum alloy containing through vanadium compound is disclosed in JP5-136978A Laid Open publication. This method is desired to obtain the surface treated film which is relatively excess in corrosion resistance of uncoated metal, however, the metal to be treated is only an aluminum alloy alone, and further it is necessary high temperature condition of 80°C. to obtain a surface treated film.

[0010] In JP5-222321A Laid Open publication, aqueous composition of treatment before coating for aluminum or aluminum alloy containing water soluble poly(methylacrylic acid or salts thereof and at least one or more than two of water soluble compound of metal selected from the group consisting of Al, Sn, Co, La, Cc and Ta is disclosed. And in JP9-254356A Laid Open publication, the surface treating composition for aluminum alloy containing organic polymer compound which contains at least one nitrogen atom or salt thereof, heavy metal or salt thereof, which is water soluble, water dispersible or emulsifiable is disclosed. These compositions are limitionally used to the surface treatment of aluminum alloy, and the performance of corrosion resistance of uncoated metal is not desirable.

surface treatment and a surface treating method for metal surface of aluminum, magnesium or zinc composed of at least one compound selected from the group consisting of metal acetylatedonate, water soluble inorganic titanium compound and water soluble inorganic zirconium compound. According to this method, it is possible to form a surface treated film having good corrosion resistance of uncoated metals. However, in said solution for surface treating of mentioned invention organic compound is used, and this organic compound can be an obstacle for establishing the closed system of water rinsing process after the film depositing treatment process.

[0012] As mentioned above, the conventional art, do not make possible to form a surface treated film which has excellent corrosion resistance of uncoated and the corrosion resistance after coated on the surface of aluminum, aluminum alloy, magnesium or magnesium alloy, using treating solution which does not discharge waste such as sludge and does not contain harmful component to the environment.

DISCLOSURE OF THE INVENTION

[0013] The object of the present invention is to provide a composition for surface treatment, a treating solution for surface treatment and a surface treating method which are aiming to form a surface treated film excels in corrosion resistance of uncoated metal and the corrosion resistance after coated on the surface of aluminum, aluminum alloy, magnesium or magnesium alloy using a treating solution which does not discharge waste such as sludge and does not contain harmful component to the environment such as hexavalent chrome. Further another object of the present invention is to provide said metal material which are excelling in corrosion resistance of uncoated metal and the corrosion resistance after coated.

[0014] The present invention is the composition for surface treatment of aluminum, aluminum alloy, magnesium or magnesium alloy comprising components (1)-(5):

[0015] (1) compound A containing at least one metal element selected from the group consisting of Hf(IV), Ti(IV) and Zr(IV),
[0016] (2) fluorine containing compound of sufficient amount to make fluorine existed in the composition at least by 5 times molarity to the total molarity of metal contained in above mentioned compound A,
[0017] (3) at least one metal ion B selected from the group of alkaline earth metal,
[0018] (4) at least one metal ion C selected from the group consisting of Al, Zn, Mg, Mn and Cu, and
[0019] (5) nitric ion.

[0020] Further, the present invention is the treating solution for surface treatment of aluminum, aluminum alloy, magnesium or magnesium alloy comprising components (1)-(5):

[0021] (1) 0.1 to 50 mmol/L of compound A containing at least one metal element selected from the group consisting of Hf(IV), Ti(IV) and Zr(IV) as said metal element,
[0022] (2) fluorine containing compound of sufficient amount to exist fluorine in the treating solution at least by 5 times molarity to the total molarity of metal contained in above mentioned compound A,
[0023] (3) at least one metal ion B selected from the group of alkaline earth metal,
[0024] (4) at least one metal ion C selected from the group consisting of Al, Zn, Mg, Mn and Cu, and
[0025] (5) nitric ion.

[0026] In above mentioned treating solution for metal surface treatment, the desirable total concentration of alkaline earth metal ion B is from 1 to 500 ppm, and desirable concentration of metal ion C is from 1 to 5000 ppm. Further, the desirable concentration of nitric ion is from 1000 to 30000 ppm. To the above mentioned treating solution for metal surface treatment, can further add at least one compound selected from the group consisting of HClO₄, HBrO₃, HNO₂, H₂MoO₄, H₂WO₄, H₂MoO₄ and oxygen acid salt thereof. And the desirable pH of the treating solution for metal surface treatment from 3 to 6.

[0027] Moreover, the present invention provides the method for metal surface treatment by contacting aluminum, aluminum alloy, magnesium or magnesium alloy with above mentioned treating solution for metal surface treatment. Further, the present invention provides the method for metal surface treatment by contacting metal material containing at least one metal selected from the group consisting of aluminum, aluminum alloy, magnesium or magnesium alloy as a component with above mentioned treating solution for metal surface treatment. Furthermore, the present invention provides the surface treated metal material comprising, possessing a surface treated film layer obtained by above mentioned method for metal surface treatment on the surface of aluminum, aluminum alloy, magnesium or magnesium alloy, wherein the coating amount of said surface treated film layer is larger than 10 mg/m² as the metal element contained in above mentioned compound A.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0028] The present invention relates to the surface treatment of aluminum, aluminum alloy, magnesium or magnesium alloy, and this surface treatment can be applied to the metal material combining at least two kind of aluminum, aluminum alloy, magnesium or magnesium alloy, further can be applied to the metal material combining at least one metal selected from the group consisting of aluminum, aluminum alloy, magnesium or magnesium alloy with a steel or a zinc plated steel. And this surface treatment is useful for the previous treatment for coating of a car body composed by these metal materials.

[0029] The composition for metal surface treatment of the present invention is the composition containing (1) compound A containing at least one metal element selected from the group consisting of Hf(IV), Ti(IV) and Zr(IV), (2) fluorine containing compound of sufficient amount to exist fluorine in the composition at least by 5 times molarity to the total molarity of metal contained in above mentioned compound A, (3) at least one metal ion B selected from the group of alkaline earth metal, (4) at least one metal ion C selected from the group consisting of Al, Zn, Mg, Mn and Cu and (5) nitric ion.
As the compound A containing at least one metal element selected from the group consisting of Hf(IV), Ti(IV) and Zr(IV) (hereinafter shortened to compound A), for example, HfCl₄, Hf(OH)₂, Hf(H₂O)₆, salt of H₂HfF₆, H₂O₂, H₂O, TiCl₄, Ti(NO₃)₂, TiF₄, salt of H₂TiF₆, Ti₂O₃, TiF₄, ZrCl₄, Zr(NO₃)₂, Zr(ZF₆)₄, H₂ZrF₆, salt of H₂ZrF₆, ZrO₂ and ZrF₄ are available. These compounds can be used together with.

As the fluorine containing compound of the component (2) of the present invention, hydrofluoric acid, H₂HfF₆, H₂F₄, H₂TiF₆, ZrF₄, H₂ZrF₆, NaH₂F₆, KHF₂, NH₄HF₂, NaF, KF and NH₄F are available. These fluorine containing compounds can be used together with.

As at least one metal ion B selected from the group of alkaline earth metal of the metal (3) (hereinafter shortened to alkaline earth metal B) is the element belonging to 2nd group of periodic law list except Be and Ra, desirably Ca, Sr or Ba. In general, although elements belonging to 2nd group of periodic law list are called as alkaline earth metals, the property of Be is different from that of other alkaline earth metal and since Be and Be compound have strong toxicity, these are out of the object of the present invention that does not contain harmful component to the environment. While, Ra is a radioactive element, and concerning it's troublesome handling, the industrial use of Ra is not so practical. Therefore, in the present invention, elements belonging to 2nd group of periodic law list except Be and Ra are used. As the supply source of alkaline earth metal ion B, oxide, hydroxide, chloride, sulfate, nitrate and carbonate of said metals can be mentioned are available.

Metal ion C of the component (4) used in the present invention, is at least one metal ion selected from the group consisting of Al, Zn, Mg, Mn and Cu (hereinafter shortened simply to metal ion C). As the supplying source of metal ion C, for example, oxide, hydroxide, chloride, sulfate, nitrate and carbonate of said metals can be mentioned. Further, as the supplying source of nitric ion of the component (5) of the present invention, nitric acid or nitrate can be used.

Practically, the composition for metal surface treatment mentioned above is diluted by water to the treating solution for metal surface treatment. This treating solution for metal surface treatment of the present invention contains at least one metal element selected from the group consisting of Hf(IV), Ti(IV) and Zr(IV) by total molar concentration of 0.1-50 mmol/L, desirably 0.2-20 mmol/L. Said metal element which is supplied from compound A in the present invention, is the main component of a surface treated film. Therefore, when the total molar concentration of said metal element is smaller than 0.1 mmol/L, the concentration of the main component of surface treated film becomes small and the enough thickness of film to perform sufficient corrosion resistance of uncoated metal and the corrosion resistance after coated can not be obtained by short treatment time. And when the total molar concentration of said metal element is larger than 50 mmol/L, although the surface treated film can be deposited sufficiently, the ability of the corrosion resistance can not be increased and is disadvantageous as is expected and it is not advantageous from the economical viewpoint.

The concentration of fluorine in fluorine containing treating solution for surface treatment of metal is at least by 5 times molarity to the total molarity of metal contained in above mentioned compound A. Desirably at least 6 times to the total molarity of above mentioned metals. The fluorine concentration is adjusted by regulating the amount of fluorine containing compound of the component (2).

The fluorine component of fluorine containing compound of the present invention has following two functions. The first one is to maintain metal elements contained in compound A of the treating solution stable in the condition of treating bath. And the second one is to etch the surface of aluminum, aluminum alloy, magnesium or magnesium alloy and to maintain aluminum ion or magnesium ion solved out into the treating solution for surface treatment stable in the treating bath.

To initiate the etching reaction of aluminum, aluminum alloy, magnesium or magnesium alloy by fluorine, it is necessary that the fluorine concentration is at least 5 times to the total molarity of metal elements contained in compound A. If the fluorine concentration is smaller than 5 times to the total molarity of metal elements contained in compound A, the fluorine in the treating solution of surface treatment is only used to maintain the stability of metal elements contained in compound A, and the sufficient etching amount can not be obtained, further, since the pH to form the oxide of above mentioned metal elements on the metal surface to be treated can not be achieved, the coating amount sufficient to perform the corrosion resistance can not be obtained.

In the case of zinc phosphate treatment, which is the conventional art, sludge is generated from the process, because, for example, aluminum ion solved out from aluminum alloy forms an insoluble salt to phosphoric acid and fluorine and sodium ion forms an insoluble salt called chlorite. On the contrary, when the treating solution for surface treatment of the present invention is used, sludge is not generated due to the solubilizing effect of fluorine. Further, when the treating amount of the metal material to be treated is remarkably large to the capacity of the treating bath, for the purpose to solubilize the solved out metal material component to be treated, an inorganic acid such as sulfuric acid, hydrochloric acid or an organic acid such as acetic acid, oxalic acid, tartaric acid, citric acid, succinic acid, gluconic acid or phthalic acid or a chelating agent which chelate metal material component to be treated can be added. These compounds can be used together with.

The metal elements provided by the compound A can exist stable in acidic aqueous solution, however, in alkaline aqueous solution said metal elements form an oxide of each metal element. Along with the etching reaction by fluorine of metal material to be treated, the pH is elevated at the surface of metal material to be treated and above mentioned metal elements forms an oxide on the metal surface to be treated. Namely, an oxide film of these metal elements is formed, and performance of the corrosion resistance is enhanced.

The component (1) and the component (2) in a composition for metal surface treatment or a treating solution for metal surface treatment display above mentioned function and form an oxide film of metal elements supplied from compound A on the surface of metal material. To these components, at least one kind of metal ion B selected from the group consisting of alkaline earth metal of the compo-
ment (3), at least one kind of metal ion C selected from the group consisting of Al, Zn, Mg, Mn and Cu of the component (4) and nitric ion of component (C) are further blended.

[0041] Generally, alkaline earth metals react with fluorine to form fluorides. Alkaline earth metal ion B in the treating solution for surface treatment of this invention generates fluoride and consumes fluorine in the treating solution for surface treatment. Along with the consumption of fluorine mentioned above, the stability of the metal element supplied from the compound A decrease. Therefore the pH value which allows to form an oxide consisting main component of film becomes lower, and it makes possible to lower the surface treatment temperature and shorter treatment time. The desirable concentration of metal ion in the solution for the metal surface treatment is 1-500 ppm and more desirable concentration is 3-100 ppm. When the concentration is lower than 1 ppm, above mentioned effect to accelerate the reaction for depositing film can not be obtained. On the contrary, when the concentration is larger than 500 ppm, the film of sufficient amount to obtain good resistance to corrosion can be obtained, however, the stability of the treating bath is spoiled. Therefore, the problem which obstruct the continuous operation is caused.

[0042] Ordinary, the fluoride of alkaline earth metal is a compound which is hard to be dissolved. One of the objects of this invention is not to generate sludge. By further blending metal ion C of the component (4) and nitric ion of the component (5) to the treating solution for metal surface treatment of the present invention, above mentioned fluoride of alkaline earth metal ion B can be solubilized and the generation of sludge can be controlled. Consequently, the reaction for film formation is accelerated and the corrosion resistance of uncoated surface can be improved.

[0043] Metal ion C is an element which generate complex fluoride. Therefore, metal ion C has the effect to consume fluorine in treating bath and to accelerate the reaction to form the treated film as well as alkaline earth metal ion B generates fluoride and consumes fluorine. Further, metal ion C has a function to solubilize alkaline earth metal ion B. Metal ion C makes fluoride of alkaline earth metal ion B solubilize by generating complex fluoride with fluorine. Furthermore, the solubility of alkaline earth metal ion B is increased by adding nitric ion. That is, by the present invention, it becomes possible to accelerate the reaction for film formation maintaining the stability of the surface treating solution by adding alkaline earth metal ion B, metal ion C and nitric ion.

[0044] The solubilizing reaction of alkaline earth metal ion B by metal ion C is illustrated as follows using example of Ca and Al as follows.

$$\text{CaF}_2 + 2\text{Al}^{3+} = \text{Ca}^{2+} + 2\text{AlF}_3$$

[0045] Still further, metal ion C has a function to improve corrosion resistance of uncoated metal. At the present time, the mechanism of improvement of corrosion resistance of metal ion C is not clear. However, the inventors have conducted intensive study about the relationship between metal to be added to the treated film formed by using compound A and corrosion resistance of uncoated metal, and has found out that the corrosion resistance of uncoated metal can be remarkably improved by adding a specific metal ion, namely metal ion C. The desirable concentration of metal ion C in the treating solution for metal surface treatment is 1-5000 ppm, and more desirable concentration is 1-3000 ppm. When the concentration is smaller than 1 ppm, the above mentioned effect to accelerate the reaction for film formation can not be obtained and the function to solubilize the fluoride of alkaline earth metal can not be obtained. And when the concentration is larger than 5000 ppm, although the formed film having sufficient amount to obtain good resistance to corrosion can be obtained, the further improving of the corrosion resistance can not be expected and is only disadvantageous economically.

[0046] Even if the concentration of nitric ion is smaller than 1000 ppm, it is possible to form the treatment film of uncoated metals has good resistance to corrosion. However, as the large amount of alkaline earth metal ion B makes the treatment solution in a bath unstable, nitric ion concentration is larger than this value. As above mentioned result, it is concluded that the desired concentration of nitric ion becomes 1000 ppm-50000 ppm. Now, the reactivity of the treating solution to metal surface can be easily survived by measuring the concentration of free fluorine ion.

[0047] Inventors conducted the measuring of concentration of fluorine ion in the treating solution to determine the desirable concentration of free fluorine ion is smaller than 500 ppm and more desirably is smaller than 300 ppm. When the concentration of free fluorine ion is larger than 500 ppm, it becomes hard to form a film having enough amount to obtain good corrosion resistance of uncoated or coated metals. These materials act as an oxidant and accelerate the above mentioned film formation reaction. In the case that these materials are used as an oxidant, the sufficient effect is obtained by adding amount of 50-50000 ppm. On the contrary, more higher concentration of these materials are needed as an etching reagent.

[0048] To the treating solution for metal surface treatment of the present invention, at least one compound selected from the group consisting of $\text{HClO}_4$, $\text{HBrO}_3$, $\text{HNO}_3$, $\text{HNO}_2$, $\text{H}_2\text{O}_2$, $\text{H}_2\text{O}_4$, $\text{H}_2\text{MoO}_6$ and salt of these oxygen acids can be added. At least one compound selected from the group consisting of above mentioned oxygen acid and salts thereof acts as an oxidant and accelerate the film forming reaction of the present invention. There is no limitation to the concentration of the above mentioned oxygen acids and salts thereof to be added, however, in the case when these are used as an oxidant, the sufficient effect is performed by the adding amount of 10-50000 ppm. Further, in the case when the above mentioned oxygen acids and salts thereof also act as the acid to maintain the etched metal material component in the treating bath, the adding amount can be increased if necessary.

[0049] The pH of the solution for metal surface treatment of the present invention is desirably to be 3-6. When the pH is lower than 3, the stability of the metal element supplied from compound A becomes stable in the solution for surface treating, and it becomes impossible to form enough amount of film to perform good corrosion resistance and resistance in the short treatment time. Further, in the case when pH is higher than 6, it is possible to form enough amount of film sufficient to obtain good resistance to corrosion, however, the film which has good corrosion resistance does not easily obtained because the treating solution becomes unstable under this pH condition.
In the present invention, the surface treated film layer can be formed on the surface of aluminum, aluminum alloy, magnesium or magnesium alloy by contacting these aluminum, aluminum alloy, magnesium or magnesium alloy with above mentioned treating solution for metal surface treatment. The desired methods are spraying method, roll coating method or dipping method. At the contact, it is desirable to set up the temperature of the treating solution for surface treatment to 30-70°C. If the treating temperature is lower than 30°C, the film formation needs longer time than conventional treatment, such as zinc phosphate treatment or chromate treatment. As zinc phosphate treatment time is two minutes or chromate treatment time is about one minute, longer treatment time than that of these treatment is not practical. On the contrary, when the temperature is higher than 70°C, it is not economically advantageous because the remarkable decreasing effect is not obtained.

Generally, it is difficult to form the uniform films on the objects composed from various kind of metals, for example car body which is composed from steel, zinc plated, aluminum alloy or magnesium alloy, because the less noble metal dissolves preferably than noble metal. And, it is very difficult to form uniform film on the surface of both two metal surfaces. The present invention proposes the countermeasure to this problem. By the method of the present invention, which dip the subject into the treating solution for metal surface treatment, alkaline earth metal ion B reacts with fluorine and generate fluoride and by said consumption of fluorine in the composition the stability of metal element of compound A in the treating bath is spoiled, therefore the pH value which make form these oxide drops. As mentioned above, since the present invention is to accelerate the film depositing reaction by adding alkaline earth metal ion B, it becomes possible to form sufficient amount of film enough to obtain the corrosion resistance on the surface metal material such as a car body characterized that the different metals are connected.

The depositing amount of surface treated film layer to the metal material to be treated of the present invention is necessary to be larger than 10mg/m² as the total amount of at least one metal element selected from the group consisting of Hf(IV), Ti(IV) and Zr(IV). In the case that depositing amount is smaller than 10 mg/m², weather the treated metal with coating has good corrosion resistance or not depends on the surface condition or components of alloys and 10 mg/m² is the threshold value to keep excellent film.

EXAMPLE

Performance of the composition for surface treatment, the treating solution for surface treatment and the method for surface treatment of the present invention will be explained in accordance to the Examples and Comparative Examples. The treated materials, a degreasing agent and a coated material other than the treating solutions of this invention are selected among the commercial materials, and in the practical treating process before coating, it is not restricted within these materials.

Test Plate

The abbreviation marks and details of the test plates used in Examples and Comparative Examples are shown as follows.

Example 1

The composition for surface treatment is prepared with aqueous solution of titanium sulfate (IV) and hydrofluoric acid. The molarity ratio of Ti to HF in the composition is 7.0 and Ti concentration is 100 mmol/L. Then Ca(NO₃)₂ reagent and ZnSO₄ reagent and HNO₃ are added, and the composition for surface treatment is prepared. The prepared composition is diluted by water and the obtained treating solution for surface treatment has Ti concentration of 50 mmol/L, Ca concentration of 2 ppm, Zn concentration of 1000 ppm and HNO₃ concentration of 1000 ppm. After degreased, a test plate is rinsed by water and kept into said treating solution adjusted to pH 4.0 using ammonium aqueous solution, at the temperature of 30°C for 180 sec.

Example 2

The composition for surface treatment is prepared with aqueous solution of hexafluorotitanic acid (IV) and hydrofluoric acid. The molarity ratio of Ti to HF in the composition is 8.0 and Ti concentration is 40 mmol/L. Then Ba(NO₃)₂ reagent, Al(OH)₃ reagent, HBrO₃ reagent and HNO₃ are added, and the composition for surface treatment is prepared.

The prepared composition is diluted by water and the treating solution for surface treatment has Ti concentration of 20 mmol/L, Ba concentration of 500 ppm, Al concentration of 20 ppm, HNO₃ concentration of 3000 ppm and HBrO₃ concentration of 500 ppm.

After degreased, a test plate is rinsed by water and kept into said treating solution adjusted to pH 4.0 using NaOH, at the temperature of 50°C for 180 sec.
Example 3
[0070] The composition for surface treatment is prepared with aqueous solution of hafnium oxide (IV) and hydrofluoric acid. The molar ratio of Hf to HF in the composition is 10.0 and Hf concentration is 30 mmol/L. Then Ca(NO$_3$)$_2$ reagent, Mg(NO$_3$)$_2$ reagent and HNO$_3$ are added, and the composition for surface treatment is prepared.

[0071] The prepared composition is diluted by water and the treating solution for surface treatment has Hf concentration of 10 m mol/L, Ca concentration of 500 ppm, Mg concentration of 250 ppm, HNO$_3$ concentration of 100 ppm and HNO$_3$ concentration of 1500 ppm.

[0072] After degreased, a test plate is rinsed by water and kept into said treating solution adjusted to pH 5.0 using ammonium aqueous solution, at the temperature at 50° C. for 60 sec.

Example 4
[0073] The composition for surface treatment is prepared by mixing aqueous solution of hexafluorozirconic acid (IV) with aqueous solution of hafnium sulfate (IV) so as the weight ratio of Zr to Hf to be Zr:HF=2:1, and hydrofluoric acid. The total molarity ratio of Zr and HF to Hf in the composition is 12.0 and total Zr and Hf concentration is 10.0 mmol/L.

[0074] This composition is diluted by water, then Sr(NO$_3$)$_2$ reagent, Mg(NO$_3$)$_2$ reagent, Mn(NO$_3$)$_2$ reagent, ZnCO$_3$ reagent, HClO$_3$ reagent, H$_2$MoO$_4$ reagent and HNO$_3$ are added, and the treating solution for surface treatment has total concentration of Zr and HF of 2 mmol/L. Sr concentration of 100 ppm, Mg concentration of 50 ppm, Mn concentration of 100 ppm, Zn concentration of 50 ppm, HClO$_3$ concentration of 150 ppm, H$_2$MoO$_4$ concentration of 300 ppm and HNO$_3$ concentration of 8000 ppm.

[0075] After degreased, a test plate is rinsed by water and said treating solution of the temperature is 45° C. whose pH is adjusted to 6.0 using KOH is sprayed to the test plate and the surface treatment is carried out for 90 sec.

Example 5
[0076] The composition for surface treatment is prepared with aqueous solution of zirconium nitrate (IV) and NH$_4$HF$_2$ reagent. The molar ratio of Zr to HF in the composition is 6.0 and Zr concentration is 10 mmol/L. Then Ca(NO$_3$)$_2$ reagent, Cu(NO$_3$)$_2$ reagent and HNO$_3$ are added, and the composition for surface treatment has Zr concentration of 0.2 mmol/L, Ca concentration of 10 ppm, Cu concentration of 1 ppm and HNO$_3$ concentration of 6000 ppm.

[0077] After degreased, a test plate is rinsed by water and kept into said treating solution adjusted to pH 5.0 using ammonium aqueous solution, maintaining the temperature at 70° C. for 60 sec.

Example 6
[0078] The composition for surface treatment is prepared with aqueous solution of hexafluoro zirconic acid (IV) and NH$_4$HF$_2$ reagent. The molarity ratio of Zr to HF is 7.0 and Zr concentration is 5.0 mmol/L. The obtained composition is diluted by water and Cu(NO$_3$)$_2$ reagent, Mg(NO$_3$)$_2$, Zn(NO$_3$)$_2$ reagent and HNO$_3$ are added, and the treating solution for surface treatment has Zr concentration of 1.0 mmol/L, Ca concentration of 1 ppm, Mg concentration of 2000 ppm, Zn concentration of 1000 ppm and HNO$_3$ concentration of 20000 ppm.

[0079] After degreased, a test plate is rinsed by water and soaked into said treating solution for surface treatment adjusted to pH 4.0 using ammonium aqueous solution, maintaining the temperature at 45° C. for 90 sec.

Example 7
[0080] The composition for surface treatment is prepared with aqueous solution of hexafluoro zirconic acid (IV) and hydrofluoric acid. The molarity ratio of Zr to HF is 7.0 and Zr concentration is 30 mmol/L. The obtained composition is diluted by water and Cu(NO$_3$)$_2$ reagent, Sr(NO$_3$)$_2$ reagent, Cu(NO$_3$)$_2$ reagent, H$_2$MoO$_4$ reagent, 35%-H$_2$O$_2$ aqueous solution and HNO$_3$ are added, and the treating solution for surface treatment has Zr concentration of 1.0 mmol/L, Ca concentration of 1 ppm, Mg concentration of 2000 ppm, Zn concentration of 30 mmol/L, Ca concentration of 150 ppm, Sr concentration of 300 ppm, Cu concentration of 2 ppm, H$_2$MoO$_4$ concentration of 1000 ppm, H$_2$O$_2$ concentration of 10 ppm, and HNO$_3$ concentration of 30000 ppm.

[0081] After degreased, a test plate is rinsed by water and said treating solution for surface treatment adjusted to pH 6.0 by NaOH, maintaining the temperature at 50° C. is sprayed and the surface treatment is carried out for 60 sec.

Example 8
[0082] The composition for surface treatment is prepared with aqueous solution of hexafluoro titanium (IV) and NaHF$_2$ reagent. The molarity ratio of Ti to HF in the composition is 7.0 and Ti concentration is 20.0 mmol/L. Then Sr(NO$_3$)$_2$ reagent, Zn(NO$_3$)$_2$ reagent, H$_2$MoO$_4$ reagent, HVO$_3$ reagent and HNO$_3$ are added, and the treating solution for surface treatment has Ti concentration is 5 mmol/L, Sr concentration of 100 ppm, Zn concentration of 5000 ppm, H$_2$MoO$_4$ concentration of 15 mmol/L, HVO$_3$ concentration of 50 ppm and HNO$_3$ concentration of 10000 ppm.

[0083] After degreased, a test plate is rinsed by water and kept into said treating solution for surface treatment adjusted to pH 3.0 using ammonium aqueous solution, maintaining the temperature at 50° C. and for 90 sec.

Comparative Example 1
[0084] The treating solution containing hafnium oxide and hydrofluoric acid in which molarity ratio of Hf to HF is 20.0 and HF concentration is 20 mmol/L is prepared. After degreased, a test plate is rinsed by water and kept into said treating solution for surface treatment adjusted to pH 3.7 using ammonium aqueous solution, maintaining the temperature at 40° C. and the surface treatment is carried out for 120 sec.

Comparative Example 2
[0085] The treating solution containing zirconium nitrate (IV) and NH$_4$HF$_2$ reagent in which molarity ratio of Zr to HF is 10.0 and Zr concentration is 0.03 mmol/L is prepared. After degreased, a test plate is rinsed by water and kept into said treating solution for surface treatment heated to 50° C.
to which corresponding amount of Ba(NO₃)₂ reagent to 10 ppm of Ba, corresponding amount of Mn(NO₃)₂ reagent to 1 ppm of Mn and further adjusted to pH 5.0 using ammonium aqueous solution and the surface treatment is carried out for 60 seconds.

Comparative Example 3

[0086] ALCHROM 713 (T.M.: product of NIHON PARKERIZING CO., LTD.), a chromic chromate treating agent, is diluted to 3.6% by tap water, then total acidity and free acidity of the prepared solution are adjusted to the center value indicated in a brochure. After degreasing, a test plate is rinsed by water and is soaked in said chromate treating solution at 35°C and kept for 60 seconds.

Comparative Example 4

[0087] PALCOAT 3756 (T.M.: product of NIHON PARKERIZING CO., LTD.), a chromic chromate treating agent, is diluted to 2% by tap water, then total acidity and free acidity of the prepared solution are adjusted to the center value indicated in a brochure. After degreasing, a test plate is rinsed by water and is soaked in said chromate treating solution at 40°C and kept for 60 seconds.

Comparative Example 5

[0088] The solution of PREPALENE ZTH (T.M.: product of NIHON PARKERIZING CO., LTD.), zinc phosphate treatment, is prepared with dilution to 0.14% by tap water. This solution is sprayed to said test plate rinsed by tap water after degreasing at room temperature for 30 sec. Then, the test plate is kept in a treating solution of zinc phosphate at 42°C which is prepared by diluting BALBOND 1.3080 (T.M.: product of NIHON PARKERIZING CO., LTD.) to 4.8% with tap water by adding 300 ppm of NaH₂PO₄ reagent as HF to adjust the total acidity and the free acidity to the center value indicated in a brochure. After this procedure the zinc phosphate film is formed on the test plate.

[0089] The prepared test plates in above mentioned Examples and Comparative Examples are tested and evaluated according to the following test procedures, that is, an evaluation of surface appearance, amount of treated film, corrosion resistance of treated film and the performance on treated plate.

[0090] Surface Appearance of Treated Film

[0091] The appearance of surface treated plate obtained in Examples and Comparative Examples are visually inspected. Results of evaluation of surface treated film are summarized in Table 1.

TABLE 1-continued

<table>
<thead>
<tr>
<th>Appearance after surface treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADC</td>
</tr>
<tr>
<td>-----------------------------------</td>
</tr>
<tr>
<td>Comp. Example 1</td>
</tr>
<tr>
<td>Comp. Example 2</td>
</tr>
<tr>
<td>Comp. Example 3</td>
</tr>
<tr>
<td>Comp. Example 4</td>
</tr>
<tr>
<td>Comp. Example 5</td>
</tr>
</tbody>
</table>

In table 1, the meaning of each abbreviated codes are indicated as follows;

U.W.C.: uniform white color,
G.C.: golden color
W.C.U.: white color uniform

[0092] Results of the test plates prepared in each Examples show that the uniform films are formed. On the contrary, in cases of Comparative Examples, an uniform film can not be formed on all test plates except Comparative Example 3 of the chromate treatment.

[0093] Amount of Surface Treated Film Layer

[0094] The amount of surface treated film layer of surface treated plates obtained in above mentioned Examples and Comparative Examples 1 and 2 are evaluated with an X-ray fluorescence analyzer (product of Rigaku Electric Industries: system 3270) by analyzing quantitatively the elements contained in the treated film. The results are summarized in Table 2.

TABLE 2

<table>
<thead>
<tr>
<th>Deposit weight per unit of surface treated film layer (total amount of Ti, Zr, HF and Si: mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADC</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>Example 1</td>
</tr>
<tr>
<td>Example 2</td>
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<tr>
<td>Example 3</td>
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<tr>
<td>Example 4</td>
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<tr>
<td>Example 5</td>
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<tr>
<td>Example 6</td>
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<tr>
<td>Example 7</td>
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<tr>
<td>Example 8</td>
</tr>
<tr>
<td>Comp. Example 1</td>
</tr>
<tr>
<td>Comp. Example 2</td>
</tr>
</tbody>
</table>

As shown in Table 2, in all cases of Example, the aimed deposit weight per unit of treated film can be obtained. While, in Comparative Examples 1 and 2, the deposit weight per unit is not attained to the aimed value.

[0095] Evaluation of Coating Performance

[0096] (1) Preparation of Test Plate

[0097] For the purpose to evaluate the coating performance of surface treated plates obtained in Examples and Comparative Examples, coating is carried out by following procedure.

[0098] cathodic electrodeposition→coating rinsing by pure water→baking→ surfacer→baking→top coating→ baking

[0099] cathodic electrodeposition coating: epoxy type cathodic electrodeposition coating (GT-10LF: product of KANSAI PAINT CO., LTD.), electric
voltage is 200 V, thickness of film is 20 μm, baked at 175° C. for 20 minutes.

[0100] surface: aminoalkyld coating (TP-65 white: product of KANSAI PAINT CO., LTD.), spray coating, thickness of film is 35 μm, baked at 140° C. for 20 minutes.

[0101] top coating: aminoalkyld coating (NEOMALAC-6000 white: product of KANSAI PAINT CO., LTD.), spray coating, thickness of film is 35 μm, baked at 140° C. for 20 minutes.

[0102] (2) Evaluation of Coating Performance

[0103] The coating performance of surface coated plates of which surface are coated by above mentioned process are evaluated. Evaluation items, evaluation method and abbreviation marks are shown below. Hereinafter, the coated film after electrodeposition coating process is called as electrodeposition coated film and the coated film after top coating is called as 3 coats coated film.

[0104] SST: salt spray test (electrodeposition coated film, and corrosion resistance after surface treatment without coating.)

[0105] The electrodeposition coated plate having cross cut lines with a sharpened knife is sprayed aqueous solution of 5%-NaCl for 840 hours (in accordance with JIS-Z-2371). After the test periods, the maximum blistering width from both side of the cross cut line is measured. While, corrosion resistance is measured by evaluating while stain generated area (%) after 48 hrs. of salt water spray without marking cross cut line by visual inspection.

[0106] SDT: hot salt water dipping test (electrodeposition coated film)

[0107] An electrodeposition coated plate having cross cut lines are marked by a sharpened knife is immersed into aqueous solution of 5%-NaCl at the temperature of 50° C. for 240 hours. After test period, rinsed by city water and dried in room temperature, the cross cut part of electrodeposition coated film is peeled using an adhesive tape, and the maximum peeled width from both side of the cross cut part is measured.

[0108] 1st ADH: primary adhesiveness (3 coats coated film, before immersion test)

[0109] 100 cross hatches of 2 mm width are marked using a sharpened knife on a 3 coats coated film. The cross hatches are peeled using an adhesive tape, and numbers of peeled hatches are counted.

[0110] 2nd ADH: water resistant secondary adhesiveness (3 coats coated film, after immersion test)

[0111] A 3 coats coated film is immersed in pure water at 40° C. for 240 hours. After immersion, 100 cross hatches of 2 mm width are marked using a sharpened knife on it. The cross hatches part is peeled using an adhesive tape, and numbers of peeled checker mark are counted.

[0112] The evaluation results of coating performance and corrosion resistance of treated material without coating are summarized in Table 3.

### Table 3

<table>
<thead>
<tr>
<th>Coating performance of electrodeposition</th>
<th>Corrosion resistance of uncoated metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>SST: max. blistering width from both side (mm)</td>
<td>SST: max. peeled width from both side (mm)</td>
</tr>
<tr>
<td>Al</td>
<td>ADC</td>
</tr>
<tr>
<td>-----</td>
<td>------</td>
</tr>
<tr>
<td>Example 1</td>
<td>0.3</td>
</tr>
<tr>
<td>Example 2</td>
<td>0.6</td>
</tr>
<tr>
<td>Example 3</td>
<td>0.4</td>
</tr>
<tr>
<td>Example 4</td>
<td>0.5</td>
</tr>
<tr>
<td>Example 5</td>
<td>0.5</td>
</tr>
<tr>
<td>Example 6</td>
<td>0.5</td>
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<tr>
<td>Example 7</td>
<td>0.5</td>
</tr>
<tr>
<td>Example 8</td>
<td>0.5</td>
</tr>
<tr>
<td>Comp.</td>
<td>0.6</td>
</tr>
</tbody>
</table>

It is obvious from Table 3 that all test plates of Examples good corrosive resistance. On the contrary, in Comparative Example 1, although the treating composition has the molarity ratio Ti to HF of 20:0, neither the alkaline earth metal ion B of the component (3) nor metal ion C of the component (4) causes the treated film unsound. Consequently, the corrosion resistance of coated plates are inferior to the test plates of Example treating. In Comparative Example 2, the sufficient amount of film can not be obtained to perform good corrosion resistance of uncoated test plate, because the concentration of Zr, which is the main component of treated film before coating, is small, 0.03 mmol/L.

Since the Comparative Example 3 is a chromate treating agent, it indicates excellent resistance to corrosion of aluminum and magnesium. Furthermore, since Comparative Example 4 is a chromium free treating agent for aluminum alloy, the corrosion resistance of aluminum is inferior to that of Comparative Example 3, relatively indicates good results. While unless the Examples are chromium free treating, they show similar ability to chromate in all items. Comparative Example 5 is a zinc phosphate treatment for aluminum simultaneous treatment which is ordinary used as the base coating for cathodic electrodeposition coating. Therefore, the resistance to corrosion of aluminum is practically good. As shown in Comparative Example 5, the corrosion resistance of Mg alloy, is inferior to that of Examples, especially, regarding to corrosion resistance of Mg alloy without coating, it can be said that not attain the desired level in practical use.

The evaluation results of adhesiveness of 3 coats plates are shown in Table 4. Examples 1-8 shows good adhesiveness to all test plates.
TABLE 4 Coating adhesiveness of 3 coats coated film

<table>
<thead>
<tr>
<th></th>
<th>1st ADH</th>
<th></th>
<th>2nd ADH</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
<td>Mg</td>
<td>Al</td>
<td>Mg</td>
</tr>
<tr>
<td>Example 1</td>
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<td>Example 2</td>
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<tr>
<td>Example 3</td>
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<td>Example 4</td>
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<td>Example 5</td>
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<td>Example 6</td>
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<td>Example 8</td>
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<tr>
<td>Comp. Example 1</td>
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<td>0</td>
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<tr>
<td>Comp. Example 2</td>
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<td>Comp. Example 3</td>
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<td>Comp. Example 4</td>
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<tr>
<td>Comp. Example 5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

According to the above mentioned results, it is obvious that the treating solution for metal surface treatment, method for surface treatment solution and surface of this invention treated metal material with the present invention, can provide a metal material with a film which has excellent corrosion resistance either uncoated or coated of aluminum, aluminum alloy, magnesium or magnesium alloy.

Further, in Comparative Example 5, sludge which is the by-product at the zinc phosphate treatment generates in the treatment both after treatment in the inventive process, the generation of sludge is not observed at every Example.

INDUSTRIAL APPLICABILITY

The treating solution for metal surface treatment and the method for surface treatment using present invention composition is the epoch-making art which makes it possible to form the surface treated film having in good corrosion resistance of metals without coating, and corrosion resistance after coating on the surface of aluminum, aluminum alloy, magnesium or magnesium alloy without generating waste such as sludge and using treating solution not containing harmful component to the environment such as hexavalent chrome.

Since the metal material for surface treatment has an excellent corrosion resistance to various environment and corrosion resistance after coated, it can be used to various fields. Furthermore, the present invention is enabled to shorten the treatment procedure and to save the operating space, because the zinc phosphate treating process usually used is not needed.

1. A composition for surface treatment of aluminum, aluminum alloy, magnesium or magnesium alloy comprising components (1) to (5):
   (1) compound a containing at least one metal element selected from the group consisting of Hf(IV), Ti(IV) and Zr(IV),
   (2) fluorine containing compound of sufficient amount to make fluorine existed in the composition at least by 5 times of molarity to the total molarity of metal contained in above mentioned compound a,
   (3) at least one metal ion b selected from the group of alkaline earth metals,
   (4) at least one metal ion c selected from the group consisting of Al, Zn, Mg, Mn and Cu, and
   (5) nitric ion.

2. A treating solution for surface treatment of aluminum, aluminum alloy, magnesium or magnesium alloy comprising components (1) to (5),
   (1) 0.1 to 50 mmol/L of compound A containing at least one metal element selected from the group consisting of Hf(IV), Ti(IV) and Zr(IV) as said metal element,
   (2) fluorine containing compound of sufficient amount to make fluorine existed in the composition at least by 5 times of molarity to the total molarity of metal contained in above mentioned compound A,
   (3) at least one metal ion B selected from the group of alkaline earth metals,
   (4) at least one metal ion C selected from the group consisting of Al, Zn, Mg, Mn and Cu, and
   (5) nitric ion.

3. The treating solution for surface treatment of aluminum, aluminum alloy, magnesium or magnesium alloy of claim 2, wherein total concentration of metal ion B is from 1 to 500 ppm.

4. The treating solution for surface treatment of aluminum, aluminum alloy, magnesium or magnesium alloy of claim 2, wherein total concentration of metal ion C is from 1 to 5000 ppm.

5. The treating solution for surface treatment of aluminum, aluminum alloy, magnesium or magnesium alloy according to claim 2, wherein the concentration of nitric ion is from 1000 to 30000 ppm.

6. The treating solution for surface treatment of aluminum, aluminum alloy, magnesium or magnesium alloy according to claim 2, to which at least one compound selected from the group consisting of HClO₄, HBrO₃, HNO₂, Hmno₃, HVO₄, H₂O₂, H₂WO₄, H₂MoO₄ and oxygen acid salt thereof are further added.

7. The treating solution for surface treatment according to claim 2, wherein the pH of the solution is 3 to 6.

8. A method for surface treatment of aluminum, aluminum alloy, magnesium or magnesium alloy comprising, contacting said metals with the treating solution for surface treatment according to claim 2.

9. A method for treatment before coating of metal materials containing at least one metal selected from the group consisting of aluminum, aluminum alloy, magnesium or magnesium alloy as the component comprising, contacting said metals with the treating solution for surface treatment according to claim 2.

10. A surface treated metal material comprising, possessing a surface treated mm layer obtained by the method for surface treatment of claim 8 on the surface of aluminum, aluminum alloy, magnesium or magnesium alloy, wherein the deposite weight per unit area of said surface treated film layer is larger than 10 mg/m² as the metal element contained in compound A.

* * * * *